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## VI.

## RESEARCHES ON THE COMPLEX INORGANIC ACIDS.

BY WOLCOTT GIBBS, M. D.,

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(Continued from Vol. XV. p. 21, June, 1879.)

Presented June 25th, 1880.

## PHOSPHO-TUNGSTATES.

THE phospho-tungstates, as already stated, were discovered by Scheibler, who gave provisional formulas for several different compounds. As the German chemist has published nothing farther upon the subject for six years, and as the study of these compounds seemed to be a necessary preliminary to that of other complex inorganic acids, I have devoted much time and labor to them. The investigation has proved very difficult and tedious, but has yielded results which, if not in all cases perfectly definite and conclusive, are yet as I think valuable and interesting. The difficulties met with in the study of this class of salts are in some respects analogous to those which present themselves in the case of the alkaline tungstates. They are mainly as follows:—

1. The normal alkaline phospho-tungstates are readily decomposed by water, yielding acid salts which are often very complex. These acid salts are very slightly soluble, and cannot in general be recrystallized for analysis. They are formed in greater or less proportion whenever we attempt to purify the neutral or less acid salts by recrystallization. In many cases the ratio of tungstic and phosphoric oxides in the neutral salt is changed when the acid salt is formed, so that we can draw no certain conclusion from the constitution of one salt as to that of the other. It is usually very difficult, or even impossible, to pass from the acid back to the primitive normal or neutral salt, because the addition of an alkali produces new compounds.

2. It is difficult by any analytical method which has been devised to determine the percentage of phosphoric oxide with great accuracy,

and very small differences — often not exceeding 0.2% — are sometimes sufficient to change the ratio between the number of atoms of phosphoric and tungstic oxides. In the case of tungstic oxide the divisor which we must employ ( $\text{WO}_3 = 232$ ) is so large that a very sensible variation in the percentage of the oxide does not sensibly affect the quotient. It is consequently sometimes difficult to decide between formulas in which, for example, the ratios of the two oxides are as 24 : 1, as 22 : 1, or as 20 : 1.

3. For similar reasons it is very difficult to recognize mixtures of different salts.

4. The alkaline phospho-tungstates are usually efflorescent, — frequently to a remarkable degree.

5. The salts of the different series agree so closely in physical and chemical properties that, as in the case of the tungstates, distinctive tests are not to be found.

6. It is almost impossible to predict what compound will be formed when tungstates and phosphates or phosphoric acid are mixed, even when the mixture is made with the greatest care and in perfectly definite proportions. Very small variations in the conditions of the process materially affect the results.

7. A large proportion of the salts of this series crystallize only from sirupy solutions, and are consequently difficult to purify by recrystallization.

8. When new salts result from a double decomposition the phospho-tungstate formed does not often correspond in composition to that from which it is derived. It may be of a higher or of a lower order.

*Preparation and General Properties.* — Scheibler prepared the salts which he has described by boiling neutral or acid sodic tungstates with half their weight of phosphoric acid. I have found it more convenient to employ the following methods. Solutions of neutral sodic tungstate,  $\text{WO}_4\text{Na}_2 + 2 \text{ aq}$ , and of hydro-disodic phosphate,  $\text{PO}_4\text{Na}_2\text{H} + 12 \text{ aq}$ , in the proportion of  $n$  molecules of the former to  $m$  of the latter, are to be boiled together for some time. The solution has a very strong alkaline reaction. It is to be neutralized with nitric or chlorhydric acid, and then contains the sodium salt — usually acid — of one or another acid of the series. As the sodium salts do not as a rule crystallize as well as those of potassium, I have sometimes found it advantageous to add a solution of potassic bromide or nitrate, when, after some hours, crystals of a potassic salt usually separate in abundance, often in fine colorless and transparent crystals. If a large excess of acid is added at once to the mixed solution of sodic tungstate

and phosphate, an acid sodium salt is often precipitated immediately, and almost always after standing a day or two. But it must be remarked that in this case the proportion of tungstic and phosphoric oxides is not always that which existed in the original mixture. In some cases I have fused the tungstate and phosphate together in definite proportions in a large platinum crucible, but this method does not present any special advantage. In other cases I have dissolved tungstic oxide in solutions of alkaline phosphates. Finally, I have in a few instances employed the original method of Scheibler. The alkaline phospho-tungstates, when not too highly acid, are usually rather easily soluble in water, but in the act of solution they almost always undergo a certain amount of decomposition, a white crystalline powder being formed which is comparatively insoluble. Sometimes the solution becomes milky at once, and remains so for a very long time. In all cases it must be allowed to stand until it becomes perfectly clear, and then poured upon the filter without disturbing the precipitate, as the filtrate would otherwise be turbid.

The alkaline phospho-tungstates are not decomposed by hydric sulphide except to a very limited extent. A current of the gas usually produces a blue color from the reduction of a small portion of the tungstic teroxide to the lower oxide  $W_2O_5$ . When an alkaline sulphide is added to a solution of a phospho-tungstate a similar reduction is produced. The addition of chlorhydric acid then gives only a small precipitate of tungstic sulphide. Zinc readily reduces a portion of the teroxide to the blue oxide, but the reduction even after some time is very far from complete. The relations of acid phospho-tungstates to salts of the various alkaloids have already been pointed out by Scheibler. In almost all cases nearly insoluble more or less distinctly crystalline precipitates are formed. I find that a beautiful heavy white crystalline salt is thrown down when an acid phospho-tungstate, as, for example, the sodium salt  $24 WO_3 \cdot P_2O_5 \cdot 2 Na_2O \cdot 4 H_2O$ , is mixed with a solution of urea, or even with urine. In this last case the precipitate contains also slightly soluble salts of potassium and ammonium. It is possible that the reaction may be utilized in animal chemistry. The phospho-tungstates also precipitate egg-albumen as a white flocky substance, which may prove to be a definite salt, in which case the high molecular weight of the acid would be of great value in determining the equivalent of the compound. I have made no experiments in this direction, and throw out the suggestion for what it may be worth.

Mercurous nitrate precipitates all the phospho-tungstates almost

completely. The yellow precipitate formed becomes more dense and compact by boiling with the supernatant liquid. It is nearly insoluble in pure water, but dissolves to some extent even in very dilute nitric acid. Dilute chlorhydric acid decomposes the salt, phospho-tungstic acid being set free. The mercurous salts of the series are the only ones which are sufficiently insoluble to be available in analysis.

Soluble salts of the different series of phospho-tungstates usually possess a strongly marked bitter taste. In a single instance the taste is at once sweet and astringent. The salts which are acid in constitution exhibit a strongly marked acid reaction.

*Analytical Methods.* — To determine the sum of the percentages of tungstic and phosphoric oxides the salt was dissolved in water or dilute nitric acid, and the two oxides precipitated together by means of mercurous nitrate with the addition of mercuric oxide, as in the estimation of tungstic oxide in the alkaline tungstates already described. This method gives good results only when used with great care, as my assistant, Dr. Gooch, observed that the high temperature and long-continued heat required to expel the whole of the mercury also drove off phosphoric oxide, so that the results frequently varied very materially, and were almost always too low. I have sometimes preferred to precipitate the two oxides with mercurous nitrate in small excess from the boiling solution, — as in the case of the tungstates, — and then to evaporate to perfect dryness on a water-bath, continuing the heat until the whole of the free nitric acid was expelled. The dry mass of mercurous phospho-tungstate and basic nitrate adheres somewhat to the evaporating dish, but not so as to render its removal very difficult. Dr. Gooch found that the adhesion was almost entirely prevented by first evaporating the solution and precipitate to a small volume, and then adding water in considerable quantity and evaporating again, this time to perfect dryness. No phosphoric oxide is vaporized on ignition for an hour at a cherry-red heat, and it is not usually necessary to ignite the mixed oxides a second time so as to insure a constant weight, though it is always better to do so. The yellow powder remaining after ignition is a mixture of tungstic oxide,  $\text{WO}_3$ , and phosphoric oxide,  $\text{P}_2\text{O}_5$ , from which water removes a portion, but not the whole, of the latter. The quantitative determination of the sum of the two oxides by this method is very nearly, but not absolutely, accurate. A trace of phosphoric acid almost always remains in the filtrate from the mercurous salt, and may be detected by evaporating this to dryness, expelling the mercurous oxide by heat, and then igniting a portion of the residue with magnesium wire. The

loss of phosphoric oxide is, however, extremely small, and probably never exceeds two or three hundredths of one per cent. The tungstic oxide was always determined by subtracting the phosphoric oxide as directly determined from the sum of the two oxides. My various attempts to determine the two oxides together by precipitation with salts of lead or barium, after neutralization with an alkali, proved failures in all cases.

The precise quantitative separation and estimation of phosphoric oxide in the phospho-tungstates is a matter of no small difficulty. After many trials of various methods, the separation by means of magnesia-mixture was found to give the best results, magnesian chloride being employed. Only, in all cases in which this method is used, it is necessary to redissolve the ammonio-magnesian phosphate first precipitated, and to precipitate the salt a second time with ammonia. The whole subject was specially investigated by Dr. F. A. Gooch, and I shall do him and the process the fullest justice by referring to his paper in Volume XV. of these Proceedings. Since the publication of Dr. Gooch's paper, I have also used in many cases the following process, which gives excellent results. The phosphoric oxide is to be precipitated in the usual manner as ammonio-magnesian phosphate, and well washed with magnesia-mixture and ammonia. The precipitate is to be redissolved in chlorhydric acid, ammonia added in small excess, and afterwards acetic acid, until the reaction is faintly but distinctly acid. The phosphoric oxide is then to be precipitated from the last solution by uranio-sodic acetate in excess. The precipitate must be allowed to settle completely, and the clear supernatant liquid poured upon the filter without disturbing the precipitate. A moderately strong solution of ammoniac nitrate is then to be added, and the precipitate again allowed to settle. After repeating this process two or three times, the precipitate may be brought upon the filter and washed with solution of ammoniac nitrate. In this manner there is no danger of obtaining a turbid or milky filtrate. After drying, the precipitate is to be ignited, moistened if necessary with nitric acid, and again ignited. This process is somewhat longer than that by double precipitation and estimation as magnesian pyrophosphate, but is, I think, rather more accurate. In almost all the analyses, by either method, the filtration and washing of the precipitate was effected by means of the asbestos filters devised by Dr. Gooch.\* It is hardly possible to speak too highly of this admirable contrivance, which in a very large number of

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\* Proceedings of American Academy, Vol. XIII. p. 342.

cases is to be preferred to any other mode of filtering, and which has been in daily use in my laboratory for nearly two years, with scarcely a single instance of failure. In many of the earlier analyses the phosphoric oxide was precipitated as ammonio-magnesian phosphate after the addition of citric acid in quantity about equal to the weight of salt taken. Dr. Gooch's later experiments showed that this method gave results which were about 8% too high when the precipitate — as was always the case — was not redissolved and thrown down a second time. In some cases I have applied this determination as a correction to the direct result of the analysis.

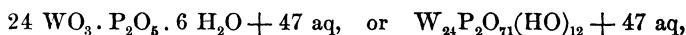
As in the analyses of the alkaline tungstates, I have usually determined the alkali by difference, making direct estimations only in doubtful cases. Ammonia was always expelled by boiling the salt with sodic hydrate, collecting in chlorhydric acid, and weighing as ammoniac chloride. Baric oxide was also sometimes estimated by difference. When precipitated from a solution of baric phospho-tungstate by sulphuric acid, the sulphate always contains phosphoric oxide, and the same is true when ammoniac carbonate and ammonia are employed. Phospho-tungstates which are insoluble in water may be resolved by fusion with an alkaline carbonate, preferably by the mixed carbonates:  $\text{CO}_3$  KNa. Water is best determined from the loss by ignition, but in some cases I have found it best to ignite with a weighed quantity of borax.

*Twenty-four Atom Series. Phospho-tungstic Acid.* — The acid is most conveniently prepared by decomposing mercurous phospho-tungstate by dilute chlorhydric acid. I have found it best to proceed as follows. To the mixture of 24 molecules of normal sodic tungstate and 2 molecules of sodic phosphate in solution, after boiling for some time, dilute nitric acid free from chlorine is to be added until the reaction is quite distinctly acid. The solution is then to be precipitated hot by mercurous nitrate in small excess, and the yellow flocky mercurous salt washed thoroughly by decantation with hot water. Toward the end of the operation a few drops of solution of mercurous nitrate may be added to the water, as the washings are otherwise apt to become milky. After washing, dilute chlorhydric acid is to be added in small quantities at a time until the yellow color disappears, and is replaced by the white of mercurous chloride. It is well to set aside a small quantity of the mercurous phospho-tungstate, and to add this to the solution of the acid so as to insure the separation of any remaining traces of chlorhydric acid. After complete subsidence the supernatant liquid is to be filtered off clear and then evaporated in vacuo over sulphuric acid. The sirupy

faintly violet liquid gives splendid large transparent crystals of phospho-tungstic acid, which are sometimes colorless and sometimes sulphur-yellow. The crystals effloresce with great rapidity, and therefore do not admit of measurement. They appear to be regular octahedra. The solution of the acid is colorless, and has a strongly acid reaction and bitter taste. Of these crystals, —

1.2791 gr. lost on ignition	0.1809 gr. water	= 14.14%
1.3005 gr. lost on ignition with fused borax	0.1842 gr. water	= 14.16%
1.4151 gr. gave	1.2130 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	= 85.72%
1.5416 gr. gave	1.3201 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	= 85.64%
1.7365 gr. gave	0.0616 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	= 2.26% $\text{P}_2\text{O}_5$

The analyses lead to the formula

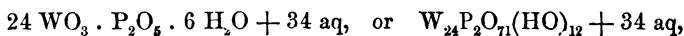


which requires: —

		Calc'd.	Mean.		
24 $\text{WO}_3$	5568	83.55	83.57	83.53	83.61
$\text{P}_2\text{O}_5$	142	2.13	2.11		2.11
53 $\text{H}_2\text{O}$	954	14.32	14.15	14.14	14.16
	<u>6664</u>	<u>100.00</u>	<u>99.83</u>		

As the phosphoric oxide in the analysis was determined after a single precipitation, a correction of 0.15 is applied to the direct result of the analysis. The crystals had slightly effloresced in drying, which explains the deficiency in the water.

A quantity of the 18-atom potassium salt  $18 \text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 6 \text{K}_2\text{O} + 26 \text{aq}$  was dissolved and precipitated by mercurous nitrate. The mercurous salt was then decomposed by dilute chlorhydric acid, and the solution of phospho-tungstic acid obtained evaporated in a flask at about  $50^\circ \text{C}$ . by means of a water air-pump, and then allowed to stand in a partial vacuum over sulphuric acid. After some days splendid colorless crystals formed, which appeared to be octahedra, but which on standing became columnar in structure, opaque, and yellow. The analyses of these crystals corresponded very closely to the formula



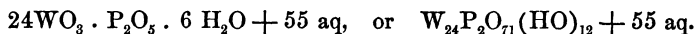
as the following analyses show: —

1.4482 gr. lost on ignition	0.1636 gr. water	= 11.30%
and gave	0.0492 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	= 2.17% $\text{P}_2\text{O}_5$
1.5109 gr. lost on ignition	0.1708 gr. water	= 11.31%
and gave	0.0521 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	= 2.20% $\text{P}_2\text{O}_5$



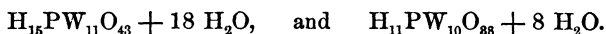
		Calc'd.		
24 WO <sub>3</sub>	5568	86.59	86.50	86.53
P <sub>2</sub> O <sub>5</sub>	142	2.20	2.20	2.17
40 H <sub>2</sub> O	720	11.21	11.30	11.31
	<u>6430</u>	<u>100.00</u>		

The yellow columnar mass, after re-solution and standing over sulphuric acid in pleno gave perfectly colorless regular octahedra, which corresponded to the formula,

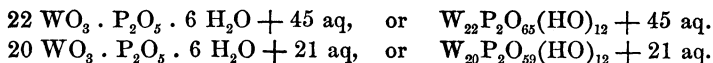


		Calc'd.		
24 WO <sub>3</sub>	5568	81.78	81.75	81.76
P <sub>2</sub> O <sub>5</sub>	142	2.08	2.14	2.15
61 H <sub>2</sub> O	1098	16.14	16.11	16.09
	<u>6808</u>	<u>100.00</u>		

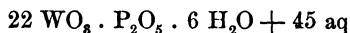
In the cases of the two last-mentioned hydrates of the acid, the phosphoric oxide was determined by two successive precipitations as ammonio-magnesian phosphate. The analyses leave no doubt as to the constitution of the acid. Scheibler obtained two different phosphotungstic acids, to which he gave respectively the provisional formulas



I should double these and write



I have not obtained the acid of the 20-atom series, though I shall show further on that there is at least one well-defined salt in which the ratio of tungstic to phosphoric oxide is as 20 to 1. Scheibler does not give the method which he employed for the separation of the two oxides, and I consider it at least probable that his acid



is identical with the first of the three hydrates which I have described above.

The solution of phosphotungstic acid forms a colorless heavy oily liquid, with a high refracting power. It has an acid as well as bitter taste, and readily expels carbonic dioxide from carbonates. On standing for some days, the solution undergoes partial decomposition with deposition of a white crystalline powder. This powder is also almost always deposited, in greater or less quantity, in the preparation of the

acid, but I could not obtain it in a state of purity sufficient for analysis. It may be worth while to note as a possible source of difference, that Scheibler obtained his acids by the decomposition of the corresponding barium salts by dilute sulphuric acid. The method of preparation which I employed is, I think, preferable.

24 : 2 *Acid Sodid Phospho-tungstate*. — When chlorhydric or nitric acid is added in large excess to a solution of normal sodic tungstate, and of hydrodisodic phosphate containing 24 molecules of the former to 2 of the latter, a salt is obtained which is usually colorless when chlorhydric acid is employed, and pale sulphur yellow when nitric acid is used. This salt crystallizes more easily than the other salts of sodium. According to Dr. Gooch, the small granular crystals appear to be either monoclinic or triclinic. They are readily soluble in water, but invariably undergo a slight decomposition in the act of solution, a small quantity of a white crystalline powder being formed which is insoluble, or but slightly soluble. The yellow and the colorless crystals have the same crystalline form and the same reactions. Their constitution is also the same, as the following analyses show:—

## I.

1.4900 gr. lost on ignition	0.1107 gr. water	= 7.43%
1.1100 gr. gave	1.0016 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	= 90.23%
1.8072 gr. “	0.0679 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	= 2.40% $\text{P}_2\text{O}_5$

## II.

0.9913 gr. lost on ignition	0.1809 gr. water	= 7.34%
0.8945 gr. “	0.0658 gr. “	= 7.32%
1.0745 gr. gave	0.9698 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	= 90.26%
1.1508 gr. “	0.0420 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	= 2.33% $\text{P}_2\text{O}_5$

## III.

1.4933 gr. lost on ignition	0.1115 gr. water	= 7.47%
1.3273 gr. gave	1.1969 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	= 90.18%
1.5424 gr. “	1.3920 gr. “	= 90.25%
1.2990 gr. “	0.0470 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	= 2.31% $\text{P}_2\text{O}_5$
1.1503 gr. “	0.0428 gr. “	= 2.38% “

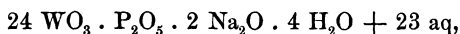
## IV.

1.8027 gr. lost on ignition	0.1349 gr. water	= 7.48%
1.1559 gr. “	0.0860 gr. “	= 7.44%
1.1269 gr. gave	1.0151 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	= 90.08%
0.9624 gr. “	0.0367 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	= 2.44% $\text{P}_2\text{O}_5$
0.6787 gr. “	0.0263 gr. “	= 2.48% “

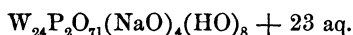
Analyses I. and II. were made with two different preparations of the colorless crystals; III. and IV. were made with the sulphur-yellow salt. The determinations of  $(\text{WO}_3 + \text{P}_2\text{O}_5)$  in I., II., and III. were made by the evaporation process without the use of mercuric oxide, but in IV. the oxide was employed. As a check upon the quantity of sodic oxide two direct determinations were made in III. the oxide being weighed as nitrate. In this manner,

$$\begin{aligned} 1.3273 \text{ gr. gave } 0.0875 \text{ gr. } \text{NO}_3\text{Na} &= 2.40\% \\ 1.2593 \text{ gr. " } 0.0924 \text{ gr. " } &= 2.68\% \text{ Na}_2\text{O} \end{aligned}$$

The mean of these two is 2.54%. As the phosphoric oxide in the analyses above cited was determined from a single precipitation as ammonio-magnesian phosphate, I have, as usual in such cases, applied a correction of 0.15% to the mean. These analyses lead to the formula



or,



		Calc'd.	Mean.							
24 $\text{WO}_3$	5568	88.10	88.04	87.98	88.08	88.02	88.02	88.09		
$\text{P}_2\text{O}_5$	142	2.25	2.24	2.25	2.18	2.16	2.13	2.29	2.33	
2 $\text{Na}_2\text{O}$	124	1.97	2.27	...	...	...	...	...	...	
27 $\text{H}_2\text{O}$	486	7.68	7.49	7.43	7.32	7.34	7.47	7.50	7.48	7.44
	6320	100.00								

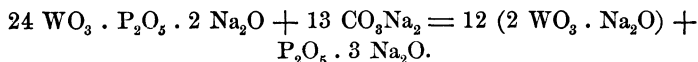
The mean of the five determinations of  $(\text{WO}_3 + \text{P}_2\text{O}_5)$  is 90.20. The formula requires 90.35. There can, I think, be no reasonable doubt as to the constitution of the acid sodium salt, though it is difficult to obtain it in a state of absolute purity. The salt is very conveniently prepared, however, and makes an excellent reagent for alkaloids. For this special purpose it is best to mix the normal tungstate and hydrodisodic phosphate in the proportion of 24 atoms of the former to 3 or 4 of the latter, boil the mixed solutions for a short time, filter, and add chlorhydric acid in excess, but in small successive portions. A precipitate is usually formed on each addition of acid which disappears on stirring the liquid. On standing, a mass of crystals of the acid salt separates. This should be drained, washed with a little cold water, then dissolved in cold water for a reagent, the clear liquid only being used.

The 24 : 2 acid phospho-tungstate of sodium appears to be always formed when an excess of chlorhydric or nitric acid is added to a so-

lution containing sodic tungstate and phosphate, in which the proportion of the latter to that of the former is as 1 to 12, or as 1 to any number less than 12. In other words, it appears to be the limiting term of all the series. When the salt is fused with sodic carbonate, carbonic dioxide is given off, but not in the proportion which might be expected. In one experiment,

$$\begin{array}{rcl} 2.2298 \text{ gr. lost } 0.5408 \text{ gr. CO}_2 \text{ and H}_2\text{O} & = & 16.94\% \\ 1.2621 \text{ gr. lost on simple ignition } 0.0922 \text{ gr. H}_2\text{O} & = & 7.31\% \end{array}$$

The ratio of the  $\text{WO}_3$  in the salt to the  $\text{CO}_2$  expelled is here as 38 : 22, or very nearly as 24 : 13. If the ratio were as 24 : 13, the reaction would be represented by the equation

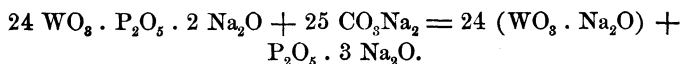


A small proportion of neutral tungstate,  $\text{WO}_4\text{Na}_2$ , is probably formed by the further action of the acid tungstate on the alkaline carbonate.

The 24 : 2 acid sodium salt gives no precipitate with the sulphates of zinc, manganese, and copper; a white crystalline precipitate with argentic nitrate, and after a short time with baric chloride and ammoniac nitrate; no precipitates with calcic and strontic chlorides, but after a short time scanty crystalline salts.

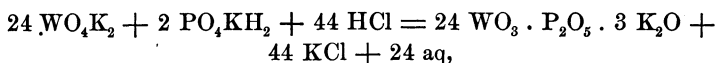
The 24 : 2 acid salt is the only sodium compound of the 24-atom series which I have been able to prepare. When a solution of this salt is carefully neutralized with sodic carbonate, the 6-atom or fully saturated salt,  $24 \text{ WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 6 \text{ Na}_2\text{O}$ , possibly exists in the solution, but a definite salt could not be obtained by evaporation. When neutral sodic tungstate and hydrodisodic phosphate are mixed in the proportion of 24 : 2, and acetic acid is added to the solution after boiling for some time, no precipitate is formed, but alcohol throws down a colorless oil which soon solidifies to a white gummy mass. I did not obtain a crystalline well-defined salt from this by re-solution and evaporation, but others may perhaps be more successful.

When a sufficient quantity of sodic carbonate is added to a solution of the acid sodic phospho-tungstate, a mixture of sodic tungstate and sodic phosphate appears to be formed.

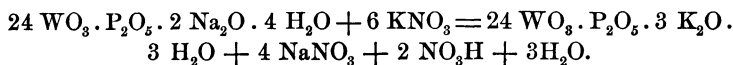


The phospho-tungstate is formed again on adding an excess of acid.

24 : 3 *Acid Potassium Salt*.—When a solution of the 24 : 2 acid sodic salt is added to one of a salt of potassium, a heavy white crystalline very slightly soluble precipitate is formed, either immediately or after a short time. The salt forms very small granular crystals. It requires a large quantity of water for solution, a white much more insoluble salt being formed in small quantity by the action of water, so that the liquid is, and for a long time remains, milky. It is best, therefore, simply to wash the precipitate with cold water until this begins to give a turbid filtrate, and then to dry the salt by pressure with woollen paper. The salt is also formed when chlorhydric or nitric acid is added to a solution of potassic phosphate and tungstate in the proportion of 2 molecules of the former to 24 molecules of the latter, — the two solutions being previously boiled together for some time in a platinum vessel. The reaction in this latter case may be expressed by the equation



and in the case of precipitation by the acid sodium salt, by the equation



In this salt, —

1.1478 gr. gave	1.0588 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	= 92.25%
1.1764 gr. “	0.0468 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	= 2.54% $\text{P}_2\text{O}_5$
1.7383 gr. lost on ignition	0.0576 gr. water	= 3.31%
1.7638 gr. “ “	0.0578 gr. “	= 3.28%

The analyses lead to the formula



		Calc'd.	Mean.	
24 $\text{WO}_3$	5568	89.93	89.86	89.86
$\text{P}_2\text{O}_5$	142	2.29	2.39	2.39 corrected.
3 $\text{K}_2\text{O}$	283	4.57	4.45	. . .
11 $\text{H}_2\text{O}$	198	3.19	3.30	3.28 3.31
	6191	100.00	100.00	

n another preparation of the same salt, —

0.7340 gr. gave	0.6660 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	= 90.74%
1.1400 gr. “	1.0317 gr. “	= 90.50%
0.8028 gr. “	0.0310 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	= 2.47% $\text{P}_2\text{O}_5$
1.5568 gr. lost on ignition	0.0805 gr. water	= 5.17%
0.8822 gr. “ “	0.0455 gr. “	= 5.16%

The analyses correspond to the formula



		Calc'd.	Mean.		
24 $\text{WO}_3$	5568	88.38	88.30	88.42	88.18
$\text{P}_2\text{O}_5$	142	2.26	2.32		2.32
3 $\text{K}_2\text{O}$	283	4.49	4.21	. . .	. . .
17 $\text{H}_2\text{O}$	306	4.87	5.17	5.16	5.17
	6299	100.00	100.00		

24 : 3 *Acid Ammonium Salt*. — When a solution of a salt of ammonium is mixed with one of sodic tungstate and phosphate, no precipitate is formed, even after standing; but if a large excess of chlorhydric or nitric acid is poured in, a white or very pale yellowish heavy crystalline salt is thrown down in large quantity. This salt is an acid phospho-tungstate of ammonia, the constitution of which varies with the proportions of the salts employed in its preparation and with the conditions of the experiment.

The different salts, however, resemble each other very closely, and may be described in the same terms. They are either perfectly white or have in mass a faint tinge of yellow and an extremely fine-grained crystalline structure. They are very slightly soluble even in hot water, and give milky emulsions which settle very slowly. Like many other phospho-tungstates and tungstates, they are difficult to wash, as they pass through the closest filter-paper with extraordinary facility. This difficulty may, however, be overcome by adding ammonic nitrate to the wash-water. The acid phospho-tungstates of ammonium are soluble in ammonia-water, but the crystals obtained from such solutions are either ammonic tungstates or salts of series different from that to which the salt dissolved belonged. They are readily decomposed by a red heat, leaving a mixture of tungstic and phosphoric oxides. When boiled with mercurous nitrate, they yield mercurous salts and ammonic nitrate.

In one preparation in which sodic tungstate and phosphate were mixed in the proportion of 20 atoms of the former to 2 of the latter, ammonic nitrate was added, and afterward nitric acid. The precipitate was washed with solution of ammonic nitrate, and afterward with alcohol and water, and dried by pressure with woollen paper. Of this salt, —

1.3460 gr. lost on ignition 0.1405 gr.  $\text{H}_2\text{O} + \text{NH}_3 = 10.44\%$   
 1.6407 gr. lost on ignition 0.1707 gr.  $\text{H}_2\text{O} + \text{NH}_3 = 10.40\%$   
 1.2038 gr. gave 0.0430 gr.  $\text{P}_2\text{O}_5 \cdot \text{Mg}_2 = 2.27\%$   $\text{P}_2\text{O}_5$  (twice precip.)  
 1.3960 gr. gave 0.0504 gr.  $\text{P}_2\text{O}_5 \cdot \text{Mg}_2 = 2.31\%$  “ “  
 1.4890 gr. gave 0.0720 gr.  $\text{NH}_4\text{Cl.} = 2.35\%$   $(\text{NH}_4)_2\text{O}$

These analyses lead to the formula



		Calc'd.	Mean.		
24 $\text{WO}_3$	5568	87.17	87.29	87.27	87.31
$\text{P}_2\text{O}_5$	142	2.22	2.29	2.27	2.31
3 $(\text{NH}_4)_2\text{O}$	156	2.44	2.35		2.35
29 $\text{H}_2\text{O}$	522	8.17	8.07	8.05	8.09
	<u>6388</u>	<u>100.00</u>	<u>100.00</u>		

It will be observed that in this case the 24-atom salt was obtained under conditions which *a priori* should have yielded a 20-atom salt. I have already stated that salts of urea are precipitated from their solutions by acid sodic phospho-tungstate  $24 \text{ WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 2 \text{ Na}_2\text{O} \cdot 4 \text{ H}_2\text{O}$ . The precipitation is, however, not complete, and the process does not appear to be available as a method of analysis.

When phosphate of aniline and 10 : 4 sodic tungstate are dissolved together, and the solution is boiled for a short time, chlorhydric acid gives an abundant yellowish-white precipitate. On re-solution the precipitate yields pale sulphur-yellow crystals, which are readily soluble in alcohol. Phosphate of para-toluidin behaves in a similar manner; the phospho-tungstate formed is readily soluble, and crystallizes in long yellow silky needles.

I did not succeed in making the insolubility of the acid ammoniac phospho-tungstate available in analysis, either for the determination of ammonia or for that of phosphoric acid. For the last-named estimation the phospho-molybdates appear to be far better adapted.

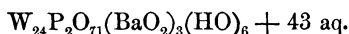
*24 : 3 Acid Barium Salt.* — When 10 : 4 sodic tungstate is dissolved and a small quantity of phosphoric acid is added, the hot solution gives with baric chloride a heavy white flocky precipitate, which readily dissolves in hot dilute chlorhydric acid. The solution, after filtration from a small quantity of flocky matter, is pale yellow, and after some time deposits splendid nearly colorless crystals, which appear to be octahedra. These are readily soluble in hot water without decomposition, and may be repeatedly recrystallized without difficulty. Of these crystals, —

0.7672 gr. gave	0.6278 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	= 81.83%
1.5557 gr. lost on ignition	0.1872 gr. water	= 12.03%
1.3732 gr. lost on ignition	0.1641 gr. water	= 11.95%
1.6196 gr. gave	0.1547 gr. $\text{SO}_4\text{Ba}$	= 6.27% $\text{BaO}$
and	0.0581 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	= 2.29% $\text{P}_2\text{O}_5$
1.2094 gr. gave	0.1158 gr. $\text{SO}_4\text{Ba}$	= 6.28% $\text{BaO}$

The analyses agree fairly well with the formula



or,



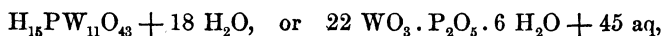
The same salt is formed when two atoms of 12 : 5 sodic tungstate are boiled for a time with two atoms of sodic phosphate and chlorhydric acid is added in excess. Baric chloride then gives after a time crystals exactly similar to those described above. In a salt prepared in this manner, —

1.0020 gr. gave	0.8173 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	= 81.56%
1.4718 gr. gave	0.1648 gr. $\text{SO}_4\text{Ba}$	= 6.97% $\text{BaO}$
and	0.0518 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	= 2.25% $\text{P}_2\text{O}_5$
1.4841 gr. lost on ignition	0.1717 gr. water	= 11.57%

		Calc'd.	Mean.		
24 $\text{WO}_3$	5568	79.57	79.57	79.69	79.46
$\text{P}_2\text{O}_5$	142	2.03	2.12	2.14	2.10
3 $\text{BaO}$	459	6.56	6.62	6.27	6.28
46 $\text{H}_2\text{O}$	828	11.84	11.78	12.03	11.95
	6977	100.00	100.09		

The phosphoric oxide determinations are corrected in both analyses. The percentage of baric oxide as determined by difference, which is the more accurate method, is 6.53. The salt effloresces with extraordinary rapidity, so that it is very difficult to dry it for analysis by pressure between folds of woollen paper.

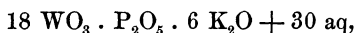
*Twenty-two Atom Series.* — The phospho-tungstates containing 22 atoms of tungstic oxide to 1 of phosphoric oxide are represented by apparently well-defined salts of potassium, sodium, and ammonium. I have not succeeded in preparing the corresponding acid. As already stated, Scheibler has given provisionally the formula



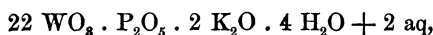


to an acid which he obtained by the decomposition of a salt of barium, and it may be that this is really the acid of the 22-atom series. Further investigations must decide the point. The salts of the 22-atom series closely resemble those of the 24-atom series already described, and are only to be distinguished from them by analysis.

22 : 2 *Potassium Salt*. — The 18-atom potassium salt,



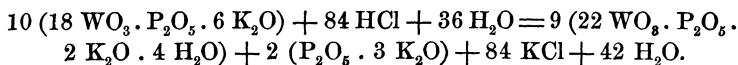
gives with chlorhydric or nitric acid a heavy white fine-granular precipitate of an acid salt which belongs to the 22-atom series, and which has the formula



as the following analyses show : —

1.5679 gr. lost on ignition	0.0318 gr. water	=	2.03%
1.0728 gr. lost on ignition	0.0222 gr. water	=	2.07%
1.5061 gr. gave	1.4250 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	=	94.61%
1.1873 gr. gave	1.1253 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	=	94.78%
2.1607 gr. gave	0.0927 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	=	2.74% $\text{P}_2\text{O}_5$
2.2367 gr. gave	0.0950 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	=	2.72% "
	Calc'd.	Mean.	
22 $\text{WO}_3$ 5104	92.08	92.11	92.20 92.03
$\text{P}_2\text{O}_5$ 142	2.56	2.58	2.59 2.57 corr.
2 $\text{K}_2\text{O}$ 189	3.41	3.26	... ..
6 $\text{H}_2\text{O}$ 108	1.95	2.05	2.03 2.07
5543	100.00		

The salt is very slightly soluble in water. The solution becomes milky, and remains so for a long time. Its formation from the normal 18-atom salt may perhaps be expressed by the equation,



22 : 3 *Ammonium Salt*. — An acid ammonium salt of this series was obtained from a mixture of sodic tungstate and phosphate, to which ammonic nitrate and excess of chlorhydric acid had been added exactly as in the preparation of the 24-atom salt already described. The salt was in very small colorless granular crystals, slightly soluble in cold water, but dissolving to some extent in hot water, giving a milky liquid, settling very slowly. Its other properties are not distinguishable from those of the 24-atom salt. Of this salt,

Gr.		Gr.		Per ct.	Per ct.
0.8697	lost on	0.0805	water and ammonia	= 9.26	= 90.73 $\text{WO}_3 + \text{P}_2\text{O}_5$
1.5911		0.1470		= 9.24	= 90.76 "
0.9086		0.0837		= 9.21	= 90.79 "
1.0934		0.1009		= 9.21	= 90.79 "
1.0934 gave		0.0439 $\text{P}_2\text{O}_7\text{Mg}_2$		= 2.63	$\text{P}_2\text{O}_5$
1.7970 "		0.0993 $\text{NH}_4\text{Cl}$		= 2.68	$(\text{NH}_4)_2\text{O}$

These analyses correspond very closely to the formula,



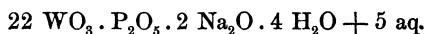
which requires:—

		Calc'd.	Mean.				
22 $\text{WO}_3$	5104	88.30	88.29	88.25	88.28	88.31	88.31
$\text{P}_2\text{O}_5$	142	2.46	2.48	2.48 corr.	...	...	...
3 $(\text{NH}_4)_2\text{O}$	156	2.69	2.68	2.68	...	...	...
21 $\text{H}_2\text{O}$	378	6.55	6.60	6.58	6.56	6.53	6.53
	5780	100.00	100.05				

**22 : 2 Sodium Salt.**—It has already been mentioned that, in the preparation of the acid sodium salt of the 24-atom series, a white very slightly soluble crystalline powder is formed in greater or less quantity. This salt cannot be recrystallized for analysis, and must therefore be washed with cold water to remove traces of the soluble acid salt. Hot water dissolves it in small proportion only, the solution remaining milky for a long time. In one preparation of this salt,—

{ 0.8405 gr. gave 0.7962 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	= 94.73%
{ 0.8405 gr. " 0.0330 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	= 2.51% { twice pre- cipitated } $\text{P}_2\text{O}_5$
1.4990 gr. lost on ignition 0.0403 gr. water	= 2.69%

These analyses lead to the formula



		Calc'd.	
22 $\text{WO}_3$	5104	92.26	92.22
$\text{P}_2\text{O}_5$	142	2.56	2.51
2 $\text{Na}_2\text{O}$	124	2.25	2.58
9 $\text{H}_2\text{O}$	162	2.93	2.69
	5532	100.00	

**22 : 4 Barium Salt.**—This salt was obtained by mixing neutral sodic tungstate and hydro-disodic phosphate in the proportion of 24 : 2, neutralizing with acetic acid, and adding a solution of baric chloride. Small sharp prismatic crystals formed after a short time, soluble in hot

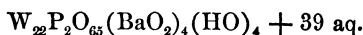
water apparently without any decomposition, and separating again from the solution in colorless needles. Of this salt, —

{	0.6900 gr.	gave 0.5494 gr.	$\text{WO}_3 + \text{P}_2\text{O}_5$	= 79.62%
{	0.6900 gr.	"	0.0826 gr. $\text{P}_2\text{O}_{11}\text{U}_2$	= 2.34% $\text{P}_2\text{O}_5$
	0.6734 gr.	"	0.5372 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	= 79.71%
	1.5296 gr.	"	0.2163 gr. $\text{SO}_4\text{Ba}$	= 9.24% $\text{BaO}$
	0.9682 gr.	lost on ignition	0.1076 gr. water	= 11.12%
	0.7064 gr.	"	"	0.0787 gr. " = 11.14%

These analyses lead to the formula



or,



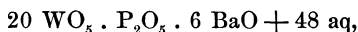
		Calc'd.	Mean.		
22 $\text{WO}_3$	5104	77.37	77.33	77.37	77.28
$\text{P}_2\text{O}_5$	142	2.15	2.34		2.34
4 $\text{BaO}$	612	9.28	9.24		9.24
41 $\text{H}_2\text{O}$	738	11.19	11.13	11.12	11.14
	<u>6596</u>	<u>100.00</u>	<u>100.04</u>		

The phosphoric oxide was precipitated twice.

*Twenty Atom Series.*—The salts of this series closely resemble those which have been described. I did not succeed in preparing the acid, though I made repeated attempts to do so by mixing sodic tungstate and phosphate together in the proportion of 20 molecules of the former to 2 of the latter, neutralizing with nitric acid, precipitating by mercurous nitrate, and decomposing the mercurous salt by dilute chlorhydric acid. The acid formed always underwent partial decomposition upon concentration, a white crystalline powder being separated while the 24-atom acid was formed. The only well-defined salt of the series which I have obtained is the normal barium compound. From this it will doubtless be possible to obtain others by double decomposition.

*Normal 20-atom Barium Salt.*—As the baric phospho-tungstates crystallize in general much more readily than the corresponding sodic salts, I employed them to determine what compounds are formed when sodic tungstate and phosphate are mixed in various proportions. To solutions of the two salts in the ratios of 24 molecules of the former to 2 of the latter, of 18 to 2, and of 12 to 2, chlorhydric acid was added until the reaction became just distinctly acid. Baric chloride was then added in excess, and the solutions were quickly filtered from the insoluble white precipitate formed. Beautiful colorless crystals

formed, which were readily soluble in hot water, and could be recrystallized without difficulty. These salts proved to have in all cases the same composition, and are represented by the formula



as the following analyses show:—

## I.

1.1103 gr. lost on ignition with fused borax	0.1458 gr. = 13.14% water.
1.1831 gr. “ “ “ “	0.1560 gr. = 13.18% “
1.0691 gr. gave	0.7775 gr. $\text{WO}_3$ and $\text{P}_2\text{O}_5$ = 72.72%
0.9390 gr. “ 0.6850 gr. “	= 72.84%

## II.

1.0676 gr. lost on ignition	0.1400 gr. = 13.11% water.
0.6550 gr. gave	0.4763 gr. $\text{WO}_3$ and $\text{P}_2\text{O}_5$ = 72.72%

## III.

1.1110 gr. lost on ignition	0.1461 gr. = 13.15% water.
0.6409 gr. gave	0.4667 gr. $\text{WO}_3$ and $\text{P}_2\text{O}_5$ = 72.81%
and	0.0704 gr. $\text{P}_2\text{O}_{11}\text{U}_2$ = 2.18% $\text{P}_2\text{O}_5$
0.6222 gr. gave	0.0710 gr. $\text{P}_2\text{O}_{11}\text{U}_2$ = 2.26% “

Analyses I. were made with the salt from the 24 to 2; II. from that obtained from the 12 to 2; and III. from the salt of the 18 to 2 mixture. The phosphoric oxide was precipitated twice.

		Calc'd.	Mean.					
20 $\text{WO}_3$	4640	70.67	70.55	70.50	70.62	70.50	70.59	
$\text{P}_2\text{O}_5$	142	2.17	2.22	...	...	...	2.18	2.26
6 BaO	918	13.99	14.09	...	...	...	...	
48 $\text{H}_2\text{O}$	864	13.17	13.14	13.14	13.18	13.11	13.15	
	6564	100.00	100.00					

The salt dissolves readily in hot water, giving a somewhat milky solution. Chlorhydric acid gives no precipitate at first, but after a time a white crystalline powder is formed, which is the acid salt of the 24-atom series already described.

The fact that the same salt is formed independently of the proportions of sodic tungstate and phosphate is an important one, and illustrates the peculiarities of the series of phospho-tungstates which I have already pointed out.

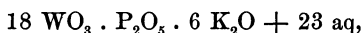
*Eighteen Atom Series.*—When normal sodic tungstate and hydrodisodic phosphate are dissolved together in the proportion of 20 molecules of the former to 2 of the latter, and acetic acid is added to

the boiling solution until a distinctly acid reaction is obtained, alcohol in excess precipitates a white indistinctly crystalline salt. This dissolves very readily in water, but gives on evaporation a gummy mass, and distinct crystals cannot be obtained. The solution of this salt gives no precipitate at first with salts of potassium, but after a short time beautiful colorless crystals are formed in abundance. The salt dissolves in a rather large excess of water, leaving a small quantity of a white insoluble compound. It crystallizes best from a solution which is not very concentrated, and which is allowed to evaporate spontaneously in the air. The crystals obtained in this way are colorless and well-defined prisms. On re-solution it almost always leaves a small quantity of the slightly soluble salt; but when the whole is dissolved together, the more soluble compound crystallizes without perceptible admixture of the other. From very concentrated solutions I obtained a white granular salt, which, on re-solution in a rather large quantity of water, gave the colorless crystals again.

Of the colorless transparent crystals,—

1.1470 gr. gave	0.9372 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	= 81.71%
1.5149 gr. “	1.2387 gr. “	= 81.77%
1.3494 gr. lost	0.1089 gr. water	= 8.07%
1.5806 gr. “	0.1277 gr. “	= 8.08%
1.1391 gr. gave	0.0498 gr. $\text{Mg}_2\text{P}_2\text{O}_7$	= 2.80% $\text{P}_2\text{O}_5$
1.1856 gr. “	0.0506 gr. “	= 2.93% “
1.5149 gr. “	0.4738 gr. $\text{AgCl}$	= 10.26% potassium.

These analyses correspond to the formula



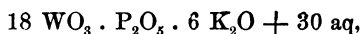
which requires:—

		Calc'd.	Mean.		
18 $\text{WO}_3$	4176	78.81	79.12	78.95	79.01
$\text{P}_2\text{O}_5$	142	2.68	2.62	2.65	2.58
6 $\text{K}_2\text{O}$	566.4	10.69	10.24		
31 $\text{H}_2\text{O}$	414	7.82	8.08	8.07	8.08
	<u>5298.4</u>	<u>100.00</u>			

Of the white granular hydrate,—

1.3868 gr. gave	1.0985 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	= 79.21%
0.9528 gr. “	0.7556 gr. “	= 79.30%
1.0396 gr. “	0.0409 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	= 2.57% $\text{P}_2\text{O}_5$
1.0614 gr. “	0.0425 gr. “	= 2.56% “
1.0102 gr. lost on ignition	0.1009 gr. water	= 9.99%
1.7974 gr. “	0.1800 gr. “	= 10.01%

The corresponding formula is



which requires —

		Calc'd.	Mean.		
18 $\text{WO}_3$	4176	76.98	76.84	76.89	76.80
$\text{P}_2\text{O}_5$	142	2.62	2.42	2.41	2.42
6 $\text{K}_2\text{O}$	566.4	10.44	10.74	...	...
30 $\text{H}_2\text{O}$	540	9.96	10.00	9.99	10.01
	<u>5424.4</u>	<u>100.00</u>			

The prismatic and granular salts, therefore, only differ in water of crystallization. It must be remarked, however, that the corrected percentages of the phosphoric oxide in the analyses of the granular salt are too low, which is unusual.

18 : 1 *Acid Potassium Salt*. — When the normal salt is dissolved in water and chlorhydric acid is added in excess, a white crystalline precipitate is formed, which is but very sparingly soluble in water. Of this salt, —

1.2955 gr. gave	1.1828 gr. $\text{WO}_3 + \text{P}_2\text{O}_5 = 91.30\%$
1.3200 gr. “	1.1994 gr. “ = 90.86%
1.1390 gr. “	0.0592 gr. $\text{P}_2\text{O}_7\text{Mg}_2 = 3.32\% \text{ P}_2\text{O}_5$
1.5900 gr. “	0.0817 gr. “ = 3.29% “
1.5225 gr. lost on ignition	0.1087 gr. water = 7.14%
1.1966 gr. “ “	0.0856 gr. “ = 7.16%

These analyses correspond to the formula



		Calc'd.	Mean.		
18 $\text{WO}_3$	4176	87.84	87.93	88.15	87.71
$\text{P}_2\text{O}_5$	142	2.99	3.15	3.17	3.14 corrected.
$\text{K}_2\text{O}$	94.4	1.98	1.77	...	...
19 $\text{H}_2\text{O}$	342	7.19	7.15	7.16	7.14
	<u>4754.4</u>	<u>100.00</u>	<u>100.00</u>		

*Ammonium Salt*. — The ammonium salt of the 18 atom series may be prepared in the manner given above for the normal potassic compound. When ammoniac acetate and alcohol are mixed with a concentrated solution of the sodium salt, no precipitate is formed at first, but after some hours a mass of white crystals is thrown down. After washing with alcohol and re-solution, crystals may sometimes be obtained, but the salt usually forms a nearly colorless gummy mass. In this case white opaque crystals separate from a thick and sirupy

mother liquor. The crystals are soft and gummy to the touch. I did not succeed in obtaining the salt in a state of purity suitable for analysis.

*Sixteen Atom Series.*—The only representatives of this series which I have obtained are salts of calcium, potassium, and ammonium. They are all well defined and more or less distinctly crystalline.

*16 : 1 Acid Calcium Salt.*—When calcic tungstate,  $\text{WO}_4\text{Ca}$ , is boiled with a pure dilute solution of phosphoric acid, the salt is dissolved very slowly; but on addition of a few drops of chlorhydric acid, the tungstate passes quickly into solution. The liquid deposits on evaporation colorless flat tabular crystals readily soluble in water. Of these crystals,—

{ 0.7356 gr. gave	0.6992 gr. $\text{WO}_3 + \text{P}_2\text{O}_5 = 95.05\%$
{ 0.7356 gr. “	0.0390 gr. $\text{P}_2\text{O}_7\text{Mg}_2 = 3.39\% \text{P}_2\text{O}_5$
1.0347 gr. lost on ignition	0.0366 gr. water = 3.54%

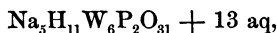
The phosphoric acid was twice precipitated. The analyses lead to the formula



which requires :—

		Calc'd.	
16 $\text{WO}_3$	3712	91.56	91.66
$\text{P}_2\text{O}_5$	142	3.50	3.39
$\text{CaO}$	56	1.38	1.41 (diff.)
8 $\text{H}_2\text{O}$	144	3.56	3.54
	<hr/> 4054	<hr/> 100.00	

*16 : 4 Acid Potassium Salt.*—In the attempt to prepare the sodium salt to which Scheibler gave provisionally the formula



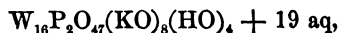
I obtained a thick sirupy liquid, which on dilution with water gave with potassic bromide, after standing a few hours, beautiful colorless needles. The salt is readily soluble in hot water. After recrystallization,—

0.5991 gr. gave	0.5000 gr. $\text{WO}_3 + \text{P}_2\text{O}_5 = 83.46\%$
2.1547 gr. “	0.1005 gr. $\text{P}_2\text{O}_7\text{Mg}_2 = 2.98\% \text{P}_2\text{O}_5$
1.0492 gr. lost on ignition	0.0841 gr. water = 8.01%

The analyses give the formula



or,



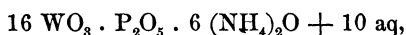
which requires : —

		Calc'd.	
16 WO <sub>3</sub>	3712	80.53	80.48
P <sub>2</sub> O <sub>5</sub>	142	3.08	2.98
4 K <sub>2</sub> O	377.6	8.19	8.53 (diff.)
21 H <sub>2</sub> O	378	8.20	8.01
	4609.6	100.00	

16:6 *Ammonium Salt*. — This beautiful salt was prepared by adding a solution of ammonic chloride to the sirupy liquid obtained by boiling 12:5 sodic tungstate with half its weight of a strong solution of pure phosphoric acid. After standing twelve hours an abundant precipitate of the ammonium salt was formed. This precipitate, after being well drained and twice recrystallized, gave very fine flat prismatic crystals. It is the best-defined ammonium salt which I have obtained. The salt is readily soluble in hot water, and crystallizes as the solution cools. Of this salt, —

1.4108 gr. lost on ignition	0.1627 gr. H <sub>2</sub> O + NH <sub>3</sub>	= 11.58%
{ 0.7705 gr. " "	0.0886 gr. " "	= 11.49%
{ 0.7705 gr. gave	0.1243 gr. P <sub>2</sub> O <sub>11</sub> U <sub>2</sub>	= 3.21% P <sub>2</sub> O <sub>5</sub>
0.9629 gr. " "	0.1430 gr. NH <sub>4</sub> Cl	= 7.17% (NH <sub>4</sub> ) <sub>2</sub> O

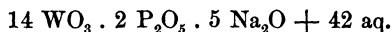
The analyses correspond with the formula



which requires : —

		Calc'd.	Mean.		
16 WO <sub>3</sub>	3712	85.41	85.28	85.30	85.26
P <sub>2</sub> O <sub>5</sub>	142	3.27	3.21		3.21
6 (NH <sub>4</sub> ) <sub>2</sub> O	312	7.18	7.17		7.17
10 H <sub>2</sub> O	180	4.14	4.34	4.32	4.36
	4346	100.00	100.00		

*Fourteen to Two Series*. — The only compound of this series which I have obtained is a sodium salt with the empirical formula



I regard this as a double salt, or perhaps as a compound of an 8-atom and a 6-atom salt.

14 : 5 *Sodium Salt*. — In the communication already referred to,\* Scheibler described briefly a sodium salt to which he gave provisionally the formula




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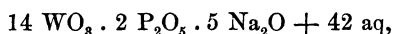
\* Berichte der Deutschen Chemischen Gesellschaft, V. 801.



This salt was obtained by boiling 12 : 5 sodic tungstate with half its weight of phosphoric acid. After a short time the salt separates in beautiful crystals. As Scheibler's salt evidently belongs to a 6-atom series, and has therefore a special theoretical interest, I endeavored in various ways to prepare it, but in all cases without success. By boiling 12 : 5 sodic tungstate with half its weight of phosphoric acid I obtained a thick sirupy liquid, which after long standing gave crystals. In another experiment about 75 gr. of the sodium salt were boiled with 13 gr. of sirupy pure phosphoric acid. After dilution and standing for some days, splendid colorless prismatic crystals separated, identical in appearance with those of the last experiment. These were redissolved and recrystallized several times. Of this salt, —

0.5551 gr. gave	0.4272 gr. $\text{WO}_3 + \text{P}_2\text{O}_5 = 76.95\%$
0.5787 gr. “	0.4459 gr. “ = 77.06%
1.5430 gr. “	1.1884 gr. “ = 77.02%
1.0058 gr. “	0.0980 gr. $\text{P}_2\text{O}_7\text{Mg}_2 = 6.35\% \text{P}_2\text{O}_5$
1.0285 gr. “	0.1014 gr. “ = 6.34% “
1.0023 gr. “	0.3214 gr. $\text{P}_2\text{O}_{11}\text{U}_2 = 6.38\%$ “
1.0152 gr. lost on ignition	0.1656 gr. water = 16.31%
1.0240 gr. “ “	0.1677 gr. “ = 16.37%
0.9922 gr. “ “	0.1612 gr. “ = 16.24%

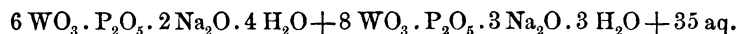
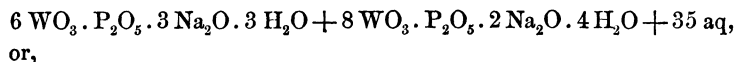
These analyses correspond fairly well to the formula



which requires : —

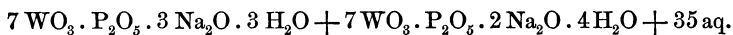
		Calc'd.	Mean.			
14 $\text{WO}_3$	3248	70.64	70.65	70.59	70.70	70.66
2 $\text{P}_2\text{O}_5$	284	6.18	6.36	6.35	6.34	6.38
5 $\text{Na}_2\text{O}$	310	6.74	6.65	. . .	. . .	. . .
42 $\text{H}_2\text{O}$	756	16.44	16.34	16.31	16.37	16.34
	4598	100.00				

The phosphoric oxide, which was twice precipitated, is too high, but it may be that in such salts a third precipitation is necessary to effect a perfect separation. I should write the formula of the salt, provisionally, either,

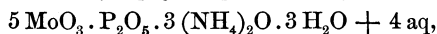


There appears to be no reason for distributing the sodic oxide in one way rather than in the other. On the other hand, it is perhaps equally

probable that the salt is a compound of two acid salts of a 7-atom series, and that its formula is



Among the corresponding phospho-molybdates there is at least one series in which the number of atoms of the teroxide is odd. Potassium and ammonium salts in this series have respectively the formulas



if, provisionally, we consider the acid as 12-basic. With respect to the formula given above, and which is that of an acid double salt, I may remark that I shall describe farther on a salt of the 5-atom molybdenum series with the formula

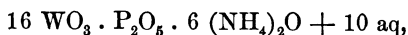


and that Rammelsberg has already described the corresponding potassium compound. From the general analogy between tungsten and molybdenum, the existence of phospho-tungstates with an uneven number of atoms of tungstic oxide may be fairly inferred from that of phospho-molybdates of the type of the 5-atom compounds above mentioned. I must leave the question undecided, for the present at least, as I have not succeeded in obtaining corresponding salts of potassium, ammonium, strontium, or calcium.

The salt crystallizes in long, flat prismatic forms, and appears to be perfectly homogeneous, so that I believe it should be regarded as a definite compound, and not as a mixture. It is very soluble in water, and crystallizes only from sirupy solutions. It has a strongly marked sweet taste, which is at the same time astringent and very slightly bitter. The solution of the sodium salt gives with potassic bromide a beautiful crystalline precipitate, already described, and having the formula



and with ammonic chloride, the ammonium salt



also noticed above.

I endeavored to obtain the normal 6-atom sodium salt  $6 \text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 6 \text{Na}_2\text{O}$  by boiling six atoms of neutral sodic tungstate with

the calculated quantity of pure phosphoric acid, but the experiment was unsuccessful.

When a solution of hydro-disodic phosphate is heated, and freshly prepared tungstic oxide is added, in small portions at a time, the oxide is readily dissolved with formation of a colorless or faintly bluish liquid. The solution gave crystalline precipitates with baric chloride and argentic nitrate, but the salts formed proved on analysis to be only mixtures. An ammonium salt was prepared by adding ammonic nitrate and nitric acid to the solution of the sodium salt. The ratio of tungstic to phosphoric oxide in the white crystalline salt formed was as 20 : 1 very closely ; but this does not lead to any inference as to the formula of the sodium salt in solution. Tribasic sodic phosphate also dissolves tungstic oxide readily, and the same is true as regards ammonic phosphate ; but I could not obtain definite salts from either solution. Potassic phosphate dissolves tungstic oxide very slowly, and only by long boiling. No definite compound was formed in this case.

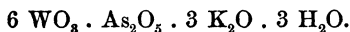
When hydro-disodic phosphate and tungstic oxide are fused together the latter dissolves and forms a colorless fused mass. This is soluble in water, but, as in the other cases, gives no single well defined salt. I have made no experiment to determine whether phospho-tungstates of the lower orders dissolve freshly precipitated tungstic oxide so as to form the higher terms in the series. The extraordinary amount of time and labor which I have already spent upon the subject must be my excuse for leaving this and many other interesting points to other investigators. There is no part of the subject which will not amply repay a new and careful study.

#### ARSENIO-TUNGSTATES.

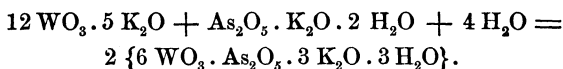
When solutions of alkaline tungstates and arsenates are mixed it frequently happens that white crystalline precipitates are formed, the supernatant liquid becoming strongly alkaline. These precipitates are arsenio-tungstates, and, as might be expected, correspond in a general way to the class of phospho-tungstates already described. They appear to be as a rule less well defined than these last, and, so far as I have been able to discover, exhibit no character of special interest. In analyzing the few salts of this series which I have studied, I have employed the same methods which I have used for the analysis of the phospho-tungstates. Only the conditions are necessarily in some respects different. Arsenic and tungstic oxides were precipitated together

by mercurous nitrate, mercuric oxide being employed to secure perfect neutrality. The mercurous salt was then separated upon an asbestos filter, and, after drying, ignited — finally with the blast-lamp — until a constant weight was obtained. In this manner very nearly the whole of the arsenic oxide was volatilized. There is no danger of a reduction to metallic arsenic if the crucible containing the asbestos and precipitate is placed within another, covered, and then cautiously heated. The arsenic oxide is best determined as ammonio-magnesian arsenate, using a large excess of magnesia-mixture in the first precipitation. Two precipitations are necessary to secure a perfect separation; the salt is to be collected on an asbestos filter, and dried in the usual manner. In determining water, or water and ammonia, in these salts, it is best to ignite with a weighed quantity of fused sodic tungstate, as suggested to me by Dr. Gooch; only it must be observed that the fused tungstate is rather deliquescent. With all these precautions fairly good results may be obtained. I endeavored to separate arsenic from tungstic oxide by boiling the salt with dilute phosphoric acid, reducing the arsenic to arsenous acid by sulphurous acid, and then precipitating by sulphydric acid as  $\text{As}_2\text{S}_3$ . This method appears to give a complete separation, but is very tedious and circumstantial.

*Acid 3-atom Potassic Arsenio-tungstate.* — When 12 : 5 acid potassic tungstate is dissolved, and a solution of potassic arsenate,  $\text{AsO}_4\text{KH}_2$ , is added, a white very fine-grained precipitate is formed. When an excess of the arsenate is employed, and the mixed solutions are evaporated upon a water-bath, a perfectly white insoluble salt is separated, which is the acid arsenio-tungstate



The formation of this salt may be represented by the equation



For analysis the salt was washed upon a filter with hot water, then dried upon paper, and afterward — as the mass remained pasty — upon a water-bath, where it finally dried to a hard white mass. Of this salt, —

0.8276 gr. gave 0.5902 gr. $\text{WO}_3$	= 71.31%
0.7197 gr. “ 0.5130 gr. “	= 71.28%
1.9815 gr. “ 0.3841 gr. $\text{As}_2\text{O}_5 \cdot \text{Mg}_2(\text{MH}_4)_2 + \text{H}_2\text{O}$	= 11.73% $\text{As}_2\text{O}_5$
1.3507 gr. lost on ignition 0.0357 gr. water	= 2.64%

The formula requires : —

		Cale'd.		
6 $\text{WO}_3$	1392	71.05	71.31	71.28
As <sub>2</sub> O <sub>5</sub>	230	11.75		11.73
3 $\text{K}_2\text{O}$	283	14.45		14.33 (diff.)
3 $\text{H}_2\text{O}$	54	2.75		2.64
	<u>1959</u>	<u>100.00</u>		

The salt dissolves readily in alkaline hydrates. Its chief interest lies in the fact that it serves to establish the existence of a 6-atom series of arsenio-tungstates.

*Acid 6 : 4 Ammonium Salt.* — When ammonic arsenate  $\text{AsO}_4\text{NH}_4$  and neutral sodic tungstate are dissolved together, no precipitate is formed at first, but after a short time a dense white crystalline salt is thrown down, which after twelve hours becomes abundant. Boiling water dissolves this salt readily, but it does not crystallize well from the solution, forming only a thick white mass. If this mass be dissolved in water, nitric acid added in excess gives a white crystalline precipitate, but slightly soluble in the acid liquid and in water. Of this salt, after washing with cold water, —

0.8255 gr. gave 0.6013 gr. $\text{WO}_3$	= 72.84%
1.9486 gr. " 0.3980 gr. $\text{As}_2\text{O}_5\text{Mg}_2(\text{NH}_4)_2 + \text{H}_2\text{O}$	= 12.36% $\text{As}_2\text{O}_5$
1.2494 gr. " 0.2635 gr. $\text{NH}_4\text{Cl}$	= 10.25%

The analyses agree — though not very closely — with the formula



which requires : —

		Cale'd.		
6 $\text{WO}_3$	1392	72.50		72.84
As <sub>2</sub> O <sub>5</sub>	230	11.98		12.36
4 $(\text{NH}_4)_2\text{O}$	208	10.83		10.25
5 $\text{H}_2\text{O}$	90	4.69		4.55 (diff.)
	<u>1920</u>	<u>100.00</u>		

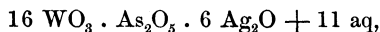
The differences are, I think, not greater than may be expected in cases in which the salt analyzed cannot be purified by recrystallization.

*Normal 16 : 6 Silver Salt.* — I obtained this salt by the following process : 100 gr. neutral sodic tungstate and 25 gr. arsenic acid were dissolved together and the solution boiled for some time, then filtered and evaporated upon a water-bath. After a day much sodic arsenate separated in crystals. The filtrate from these crystals deposited a

white indistinctly crystalline mass. This was redissolved and potassic bromide added in excess, when an abundant white crystalline fine-grained precipitate was thrown down, which was drained on the filter-pump, and then washed with cold water. This was dissolved in much boiling water, and argentic nitrate added, when a white crystalline salt was thrown down mixed with brownish-red crystals of argentic arsenate. The mass was treated with very dilute nitric acid, which readily dissolved the arsenate, the undissolved portion appearing under a lens as made up of opaque white acicular crystals. These were well drained, washed with cold water, and dried on paper by pressure, when the mass showed a faint yellowish tint. The salt is but slightly soluble in cold water. Of this salt, —

0.7488 gr. gave	0.5024 gr. $\text{WO}_3$ = 67.09%
0.7531 gr. “	0.5067 gr. “ = 67.29%
2.0321 gr. “	0.6147 gr. $\text{AgCl}$ = 24.45% $\text{Ag}_2\text{O}$
1.0215 gr. “	0.3096 gr. “ = 24.48% “
0.9209 gr. lost on ignition	0.0340 gr. water = 3.69%

The analyses correspond tolerably well to the formula



which requires: —

		Calc'd.		
16 $\text{WO}_3$	3712	67.10	67.09	67.29
$\text{As}_2\text{O}_5$	230	4.16		4.65 (diff.)
6 $\text{Ag}_2\text{O}$	1392	25.16	24.45	24.48
11 $\text{H}_2\text{O}$	198	3.58		3.69
	<u>5532</u>	<u>100.00</u>		

I do not place implicit confidence in the formula given, as the two determinations of argentic oxide are too low. It is very possible that the salt was slightly decomposed by the dilute nitric acid employed to remove the arsenate. But in any case it is proved that arsenio-tungstates exist in which the ratio of  $\text{WO}_3$  to  $\text{As}_2\text{O}_5$  is higher than 6 : 1, and a method of obtaining such compounds is pointed out.

*General Conclusions.* — The general results of my investigation of the phospho-tungstates may be stated briefly as follows: —

1. The phospho-tungstates form a series of which the lowest term probably contains six atoms of tungstic to one of phosphoric oxide, and the highest, twenty-four atoms of tungstic to one of phosphoric oxide.

2. At least the greater number of phospho-tungstates contain an even number of atoms of tungstic oxide. The homologizing term for these cases is therefore  $2 \text{WO}_3$ .

3. The highest number of atoms of base observed in any case is six (old style), which implies that each acid contains twelve atoms of hydroxyl.

4. In all cases observed the number of atoms of hydroxyl replaced by a monatomic metal is even.

5. One instance occurs in which two acid phospho-tungstates of different orders appear to unite to form a definite compound; but this case admits of a different explanation.

6. In all phospho-tungstates studied the number of atoms of base or of hydroxyl is more than sufficient to saturate the phosphoric oxide present, if we admit that the acid is 12-basic. At least a part of the hydroxyl or base must therefore be united to tungstic oxide.

For greater facility of comparison I have brought together the formulas of all the compounds described in this paper, writing them both with the old and the new notation.

24 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 6 \text{H}_2\text{O} + 47 \text{ aq}$	$\text{W}_{24}\text{P}_2\text{O}_{71}(\text{HO})_{12} + 47 \text{ aq}$
24 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 6 \text{H}_2\text{O} + 34 \text{ aq}$	$\text{W}_{24}\text{P}_2\text{O}_{71}(\text{HO})_{12} + 34 \text{ aq}$
24 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 6 \text{H}_2\text{O} + 55 \text{ aq}$	$\text{W}_{24}\text{P}_2\text{O}_{71}(\text{HO})_{12} + 55 \text{ aq}$
24 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 2 \text{Na}_2\text{O} \cdot 4 \text{H}_2\text{O} + 23 \text{ aq}$	$\text{W}_{24}\text{P}_2\text{O}_{71}(\text{NaO})_4(\text{HO})_8 + 23 \text{ aq}$
24 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 3 \text{K}_2\text{O} \cdot 3 \text{H}_2\text{O} + 8 \text{ aq}$	$\text{W}_{24}\text{P}_2\text{O}_{71}(\text{KO})_6(\text{HO})_6 + 8 \text{ aq}$
24 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 3 \text{K}_2\text{O} \cdot 3 \text{H}_2\text{O} + 14 \text{ aq}$	$\text{W}_{24}\text{P}_2\text{O}_{71}(\text{KO})_6(\text{HO})_6 + 14 \text{ aq}$
24 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 3 (\text{NH}_4)_2\text{O} \cdot 3 \text{H}_2\text{O} + 26 \text{ aq}$	$\text{W}_{24}\text{P}_2\text{O}_{71}(\text{NH}_4\text{O})_6(\text{HO})_6 + 26 \text{ aq}$
24 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 3 \text{BaO} \cdot 3 \text{H}_2\text{O} + 43 \text{ aq}$	$\text{W}_{24}\text{P}_2\text{O}_{71}(\text{BaO})_3(\text{HO})_6 + 43 \text{ aq}$
22 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 2 \text{K}_2\text{O} \cdot 4 \text{H}_2\text{O} + 2 \text{ aq}$	$\text{W}_{22}\text{P}_2\text{O}_{65}(\text{KO})_4(\text{HO})_8 + 2 \text{ aq}$
22 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 3 (\text{NH}_4)_2\text{O} \cdot 3 \text{H}_2\text{O} + 18 \text{ aq}$	$\text{W}_{22}\text{P}_2\text{O}_{65}(\text{NH}_4\text{O})_6(\text{HO})_8 + 18 \text{ aq}$
22 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 2 \text{Na}_2\text{O} \cdot 4 \text{H}_2\text{O} + 5 \text{ aq}$	$\text{W}_{22}\text{P}_2\text{O}_{65}(\text{NaO})_4(\text{HO})_8 + 5 \text{ aq}$
22 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 4 \text{BaO} \cdot 2 \text{H}_2\text{O} + 39 \text{ aq}$	$\text{W}_{22}\text{P}_2\text{O}_{65}(\text{BaO})_4(\text{HO})_4 + 39 \text{ aq}$
20 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 6 \text{BaO} + 48 \text{ aq}$	$\text{W}_{20}\text{P}_2\text{O}_{59}(\text{BaO})_6 + 48 \text{ aq}$
18 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 6 \text{K}_2\text{O} + 23 \text{ aq}$	$\text{W}_{18}\text{P}_2\text{O}_{58}(\text{KO})_{12} + 23 \text{ aq}$
18 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 6 \text{K}_2\text{O} + 30 \text{ aq}$	$\text{W}_{18}\text{P}_2\text{O}_{58}(\text{KO})_{12} + 30 \text{ aq}$
18 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot \text{K}_2\text{O} \cdot 5 \text{H}_2\text{O} + 14 \text{ aq}$	$\text{W}_{18}\text{P}_2\text{O}_{58}(\text{KO})_2(\text{HO})_{10} + 14 \text{ aq}$
16 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot \text{CaO} \cdot 5 \text{H}_2\text{O} + 3 \text{ aq}$	$\text{W}_{16}\text{P}_2\text{O}_{47}(\text{CaO})_1(\text{HO})_{10} + 3 \text{ aq}$
16 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 4 \text{K}_2\text{O} \cdot 2 \text{H}_2\text{O} + 19 \text{ aq}$	$\text{W}_{16}\text{P}_2\text{O}_{47}(\text{KO})_8(\text{HO})_4 + 19 \text{ aq}$
16 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 6 (\text{NH}_4)_2\text{O} + 10 \text{ aq}$	$\text{W}_{16}\text{P}_2\text{O}_{47}(\text{NH}_4\text{O})_{12} + 10 \text{ aq}$
14 $\text{WO}_3 \cdot 2 \text{P}_2\text{O}_5 \cdot 5 \text{Na}_2\text{O} + 42 \text{ aq}$	
6 $\text{WO}_3 \cdot \text{As}_2\text{O}_5 \cdot 3 \text{K}_2\text{O} \cdot 3 \text{H}_2\text{O}$	$\text{W}_6\text{As}_2\text{O}_{27}(\text{KO})_6(\text{HO})_6$
6 $\text{WO}_3 \cdot \text{As}_2\text{O}_5 \cdot 4 (\text{NH}_4)_2\text{O} \cdot 2 \text{H}_2\text{O} + 3 \text{ aq}$	$\text{W}_6\text{As}_2\text{O}_{27}(\text{NH}_4\text{O})_8(\text{HO})_4 + 3 \text{ aq}$
16 $\text{WO}_3 \cdot \text{As}_2\text{O}_5 \cdot 6 \text{Ag}_2\text{O} + 11 \text{ aq}$	$\text{W}_{16}\text{As}_2\text{O}_{47}(\text{AgO})_{12} + 11 \text{ aq}$

In writing these formulas I have assumed that *all* the acids are 12-basic, since it has been shown that there are salts of the sixteen-, eighteen-, and twenty-atom series which correspond with this view. I shall resume the discussion of the subject in connection with the phospho-molybdates, and at the same time examine in detail the question of the existence of a distinct class of pyro-salts of the tungstic and molybdic series.

*(To be continued.)*